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SAND97-0830 • UC-704

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Printed May 1997

LDRD Final Report on Nanocomposite Materials Based on Hydrocarbon-Bridged Siloxanes

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**LDRD Final Report on
Nanocomposite Materials Based on Hydrocarbon-Bridged Siloxanes**

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Abstract

Silicones [polydimethylsiloxane (PDMS) polymers] are environmentally safe, nonflammable, weather resistant, thermally stable, low T_g materials which are attractive for general elastomer applications because of their safety and their performance over a wide temperature range. However, PDMS is inherently weak due to its low glass transition temperature (T_g) and lack of stress crystallization. The major goal of this project was to create a family of reinforced elastomers based on silsesquioxane/PDMS networks. Polydimethylsiloxane-based (PDMS) composite materials containing a variety of alkylene- and arylene-bridged polysilsesquioxanes were synthesized in order to probe short chain and linkage effects in bimodal polymer networks. Monte Carlo simulations on the alkylene-bridged silsesquioxane/PDMS system predicted that the introduction of the silsesquioxane short chains into the long chain PDMS network would have a significant reinforcing effect on the elastomer. The silsesquioxane-PDMS networks were synthesized and evaluated. Analysis of the mechanical properties of the resulting materials indicated that use of the appropriate silsesquioxane generated materials with greatly enhanced properties. Arylene and activated alkylene systems resulted in materials that showed superior adhesive strength for metal-to-metal adhesion.

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Introduction

Using the silsesquioxanes, we introduced and varied the alkylene and arylene linkages, in order to probe the concept of short-chain toughening. (Fig. 1)

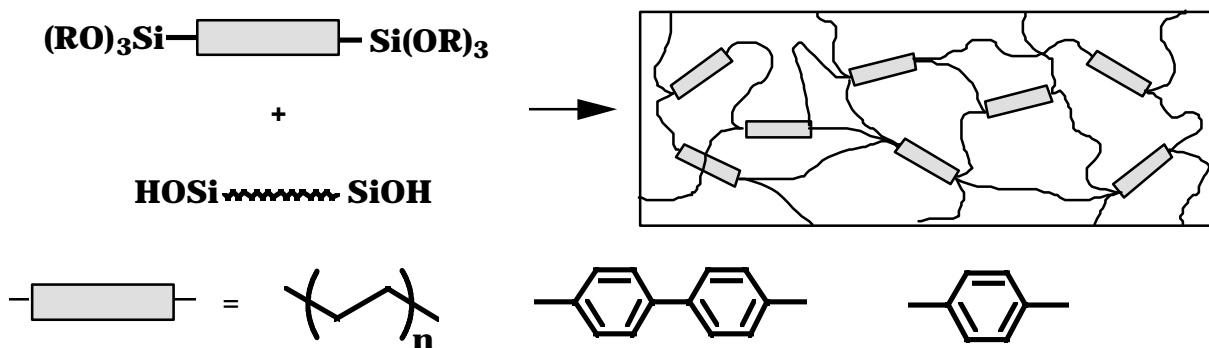


Figure 1. Preparation of silsesquioxane/PDMS bimodal materials.

Monte Carlo simulations were performed on the PDMS and alkylene-bridged silsesquioxane chains as a function of chain length to determine the strain energy and force extension behavior of the single chain species. This information was used to predict the stress strain behavior of the resulting bimodal networks.⁴

In order to understand the macromolecular and molecular structure, the polymer blends were evaluated by Scanning Electron Microscopy (SEM) and by solid state ²⁹Si NMR. In addition, simple mechanical measurements, such as tensile strength, elongation and durometer were completed. Finally, an evaluation of the suitability of the materials for microcircuit encapsulation and adhesive applications was completed.

Results and Discussion

Silsesquioxane or Short-Chain Monomers. In order to explore structural and electronic effects of the short chain component, the ethylene-, propylene-, hexylene-, octylene-, decylene-, phenylene-, and biphenylene-bridged triethoxysilanes (or silsesquioxanes) were synthesized and purified. The propylene-, hexylene-, and phenylene-bridged diethoxymethylsilanes were also prepared. The alkylene-bridged monomers were prepared by hydrosilylation of the appropriate α , ω -dienes. The arylene-bridged monomers were prepared by Barbier Grignards from the aryldibromides and tetraethoxysilane, methyltriethoxysilane, or tetramethoxysilane.

Before composite materials could be made, the effectiveness and relative reactivity of the monomers to the tin catalysts normally used in silicone formulations was determined by examining two representative monomers. The arylene- and alkylene-based systems were represented by the phenylene and hexylene bridges, respectively, and both the methoxy and ethoxy derivatized systems were utilized. Two tin catalysts, dibutyltin dilaurate (a tin(IV) catalyst of moderate activity) and tin octoate (a tin(II) catalyst of high activity), were examined. Only the higher activity catalyst, tin octoate, was effective. It was found that arylene/methoxy system gelled in 8 hours, leading to a white gel. In contrast, the hexylene/methoxy system was found to be much more reactive and yielded a white gel in less than a half hour. Comparing the ethoxy systems, the phenylene system was found to be nonreactive and never formed a gel while the hexylene system formed a translucent blue gel within 48 hours.

In order to understand the observed differences in reactivity, the above systems were further investigated by solution and solid state ²⁹Si NMR. Using 1 molar solutions with 1 equivalent of water, we found that the hexylene/ethoxy system showed initial hydrolysis and condensation had occurred within 15 minutes and appreciable reactivity was displayed within 24 hours. In contrast, the phenylene/ethoxy system displayed no signs of either hydrolysis or condensation in 24 hours. Solid state ²⁹Si NMR of the gels did not show anything unusual in the silicon atom environment distribution compared to gels normally formed by acid catalysis.

Bimodal Systems. Knowing that tin octoate was an effective catalyst, we then synthesized silsesquioxane/siloxane nanocomposite materials. Even though the homopolymerization studies indicated that the alkylene systems were far more reactive with tin octoate than the arylene monomers, initial attempts to form composite materials were carried out with both representative monomers. Surprisingly, this led to very weak materials with the hexylene species and high strength arylene-based materials. Further

synthesis looked at an entire range of composite materials, utilizing PDMS with molecular weights ranging from 800 to 700,000 and alkylene systems from ethylene (C₂) to tetradecylene (C₁₄) and 0.3 wt% tin octoate. All of the samples were cured in a 65% relative humidity chamber at room temperature for one week. It was found that using PDMS of too low a molecular weight led to extremely brittle materials. If too high a molecular weight of PDMS was used, the silsesquioxane could not be mixed into the polymer. PDMS with a molecular weight in the 20,000 to 40,000 range with arylene-based silsesquioxanes led to the best properties. (Table 1)

Table 1. Mechanical Properties of Arylene vs Alkylene Composites at 5% Silsesquioxane.

Bridging Group	PDMS (MW)	Tensile (psi)	Elongation (%)	Shore A Dur.
Biphenylene	23,080	707	132	54
Phenylene	19,800	667	232	55
Ethylene	19,800	***	***	***
Ethylene	37,900	56	208	27
Hexylene	19,800	45	155	24
Hexylene	37,900	41	241	19
Tetradecylene	19,800	48	135	29
Tetradecylene	37,900	171	252	35

*** - sample did not cure

Examination of the cured samples by ²⁹Si solid state NMR showed that appreciable hydrolysis and condensation only occurred in the arylene systems. The alkylene systems apparently reacted only enough to generate a cured sample since no hydrolysis and condensation products were detectable within the limits of the experiment.

In order to examine the effect of the amount of the short chain moiety on the mechanical properties, a series of arylene-based samples were synthesized at various silsesquioxane loadings. (Table 2)

Table 2. Mechanical Properties of Arylene Composites with PDMS (23,100 MW) at Varying Silsesquioxane Loading Levels.

Bridging Group	Loading	Appearance	Tensile (psi)	Elongation (%)	Shore A Dur.
Phenylene	Stoich.	clear	80	172	26
Phenylene	5%	translucent	667	232	55
Biphenylene	5%	white	707	132	53/54
Biphenylene	10%	white	664	53	70/75
Biphenylene	15%	white/layered	****	****	68/80
Biphenylene	20%	white/layered	****	****	35/60

**** - too brittle to measure

An examination of the mechanical properties shows that the silsesquioxane provides appreciable reinforcement if it is at the right loading level. However, if too high a loading of the short chain species is used, gross phase separation begins to occur, as indicated by the layered appearance of the samples and the marked difference in the hardness of the samples on their top and bottom. This phase separation is accompanied by a dramatic decrease in the properties due to embrittlement.

In an attempt to discover why the arylene systems were surprisingly better in reactivity in the composite system when the homopolymerizations had overwhelmingly indicated that the alkylene systems were superior, the miscibility of the silsesquioxanes in the PDMS was investigated. (Table 3)

Table 3. Miscibilities of Silsesquioxanes with PDMS

Monomer	Miscible	Redissolve
Phenylene/Methoxy	Yes	Not Applicable
Phenylene/Ethoxy	Yes	Not Applicable
Hexylene/Methoxy	Gel	No
Hexylene/Ethoxy	Gel	No

The monomers were mixed with neat PDMS (853 MW) and allowed to stand in the absence of catalyst. If turbidity resulted or a gel formed, tetrahydrofuran was added in an attempt to redissolve the gel. It was determined that the phenylene systems are completely miscible with PDMS, while the alkylene systems form a physical gel which can not be redissolved. This nonmiscibility is presumably what leads to the poor reactivity and poor properties observed for the alkylene-based composites. Attempts to use solvents as miscibilizing agents during composite synthesis were relatively unsuccessful. A moderate increase in properties was achieved with approximately 30% to 40% solvent addition, however properties comparable with the arylene systems were not obtained.

In order to change the miscibility and reactivity of the alkylene systems, the effectiveness of partial precondensation was investigated. Although precondensation is not suitable for all of the monomers, it is very effective for some of them. For instance, the ethylene bridged species can be easily precondensed. This precondensed monomer when combined with PDMS (23,100 MW) at 10% loading generated composite materials with dramatically increased mechanical properties. (Table 4)

Table 4. Effect of Monomer Precondensation

Monomer	Appearance	Tensile (psi)	Elongation (%)	Shore A Dur.
Ethylene/Ethoxy	clear	61	66	38/40
Precondensed-Ethylene/Ethoxy	slightly opaque	822	132	58/60

^{29}Si solid state NMR indicated that the precondensed monomer led to a material as fully reacted as the arylene systems. Therefore, it appears that, when applicable, precondensation is a very effective means of increasing the reactivity and miscibility of the silsesquioxanes with PDMS.

Calculations. Monte Carlo simulations were completed on the alkylene-bridged silsesquioxane/PDMS system to predict the ultimate properties of the bimodal systems. These simulation studies indicated that the introduction of the silsesquioxane short chains into the long chain PDMS network would have a significant reinforcing effect on the elastomer. This reinforcement increased as more short chains were introduced. However, there was a trade-off in properties, in that the ultimate elongation is predicted to decrease as the short chains get shorter and as more short chains are introduced. It should be noted that these predictions assume that the system does not phase separate during synthesis. The SEM and scattering data indicate that this assumption is not always valid. While these predictions have not been completely verified, we have seen that there is an optimum amount of filler/crosslinking. Beyond this amount of "short chain" the samples become too brittle for usefulness.

Applications. The composite materials were tested for two weapon related applications, electronic packaging and metal-to-metal adhesives. The materials were tested as encapsulants for nonhermetic electronic packaging and showed few failures during temperature cycling under high humidity conditions. However, initial studies did not show them to be demonstrably better than commercial silicone materials. The materials did demonstrate a five-fold improvement in adhesive strength when compared to commercial adhesives currently used in weapons.

Conclusions

The completion of the LDRD project "Nanocomposite Materials Based on Hydrocarbon-Bridged Siloxanes" demonstrated that the silsesquioxane monomers are effective reagents for reinforcing PDMS. Problems with miscibility can be relieved partially by adding miscibilizing solvents and dramatically relieved by carrying out precondensation reactions.

Important factors for the successful generation of silsesquioxane-PDMS composite materials are the relative rates of reaction or condensation, the nature of the hydrocarbon-bridging group, the PDMS molecular weight, the loading level of the monomer, and the overall miscibility of the system. The resulting composite materials were found to be best suited for metal-to-metal adhesive applications.

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Acknowledgments

Several people contributed greatly to this project. Dr. Eric Black, a postdoctoral fellow (now with Georgia-Pacific) completed the very initial composite synthesis. Prof. Ken Shea (U. C. Irvine) provided monomer synthesis, along with work at SNL by Duane Schneider and Brigitta Baugher. SEM characterization was done by Gary Zender and NMR characterization was completed by Dr. Roger Assink and Dr. Todd Alam. Adhesion and encapsulation testing were completed by David Zamora.

Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the U. S. Department of Energy. This work was supported by the Laboratory Directed Research and Development Program under contract DE-AC04-94AL8500.

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